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Metal-Ligand Equilibria in Solution: A Generalized Approach

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A new approach for the evaluation of the equilibrium constants of various types of metal-ligand equilibria has been discussed. For the non-protonated, protonated and the hydroxo complexes, the stability constants have been calculated. The methods of calculation have also been extended to the determination of equilibrium constants of the mixed complexes involving several ligands which have comparable affinity for complex formation with the metal ion. A general formula $\sum_{m=1}^{m=n+1} S_m[A]^m = S_{n+2}$ has been obtained for the free ligand concentration, where n is the maximum number of ligands attached to metal ion and $S_1, S_2, \ldots, S_{n+2}$ are the constants which can be determined from the experimental data.

THE literature on investigations of metal-ligand equilibria in solution employing various techniques almost defies a comprehensive examination[1]. The use of the *p*H-metric method[2-4] is popular and the equilibrium constants are obtained by calculating Bjerrum functions $\bar{n}_A$, $\bar{n}$ and free ligand exponent, *p*L. The method of Chaberek and Martell[5] is more informative from structural point of view and may be applied to evaluate the formation and dissociation constants of the protonated chelate species and formation constants of hydroxo, mixed, and polymeric species as well. However since no mineral acid was added to the mixtures for titration, the state of affairs at low *p*H ranges could not be known.

It was, therefore, considered necessary to modify this method of Chaberek and Martell and to add a mineral acid to the titration mixture before titrating against a standard alkali solution. This modified method was applied to several systems[6-8] and the results were encouraging. In this paper a general and comprehensive treatment of the various types of equilibria in metal-ligand systems has been considered and expressions for obtaining the equilibrium constants corresponding to the different types of situations have been attempted.

Titrations

The following mixtures for titration against a standard alkali were prepared:

(i) Perchloric acid solution, (ii) perchloric acid + ligand solution, and (iii) mixture (ii) + metal ion solution. All the concentrations were known and total volume was kept constant. A number of mixtures (iii) were obtained, so that metal to ligand ratios were 1:0·5, 1:1, 1:2, etc. Titration curves showing the variation of *p*H against volume of alkali added are shown in Fig. 1. At any *p*H, v_1 and v_2 are the volumes of alkali used in the acid, and (acid+ligand) titration curves respectively. Similarly v_3 represents the volume of alkali for the (acid+ligand+metal ion) system. On varying the metal:ligand ratios (i.e. 1:0·5, 1:1, 1:2 etc. depending upon the experimental requirements) the number of moles of alkali used per mole of ligand or metal (a) can be obtained from the values of (v_2-v_1) and (v_3-v_1) read from the curves. The a vs *p*H curves respectively for proton-ligand (Fig. 2) and metal-ligand (Fig. 3) equilibria similar to those discussed

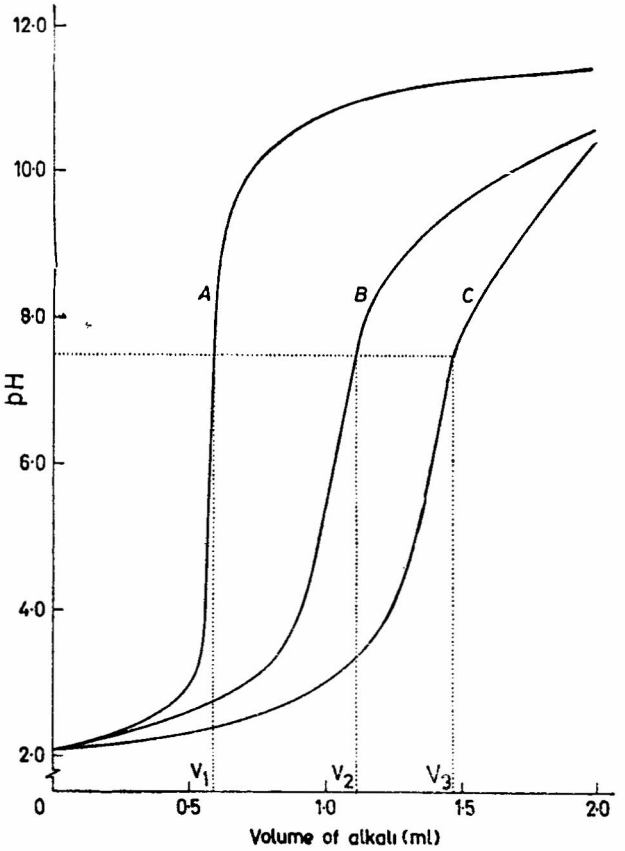

Fig. 1 — Titration curves-volume of alkali vs *p*H [*A*: $HClO_4$; *B*: $HClO_4$ + ligand (H_nA); *C*, $HClO_4$ + H_nA +metal ion]

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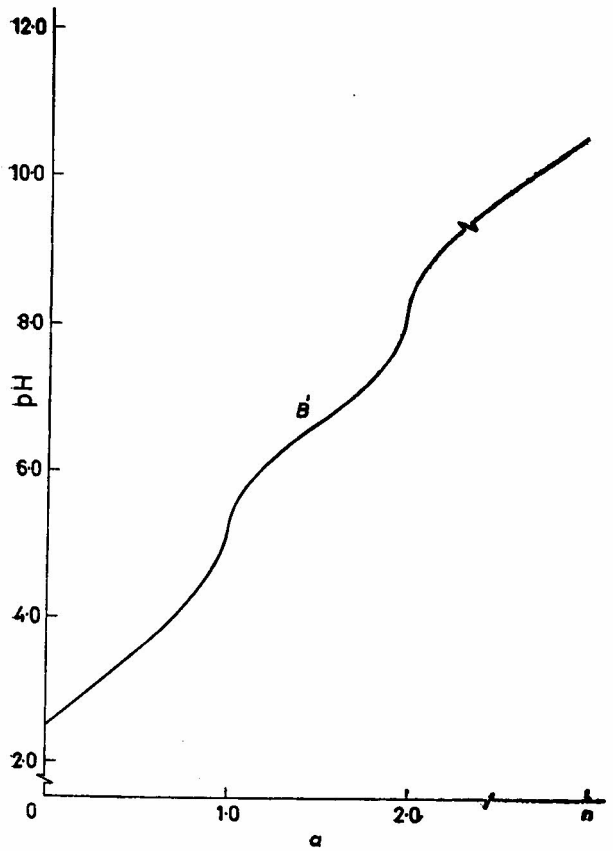

Fig. 2 — Titration curve for the ligand (H_nA) — moles of alkali used per mole of ligand (a) vs pH

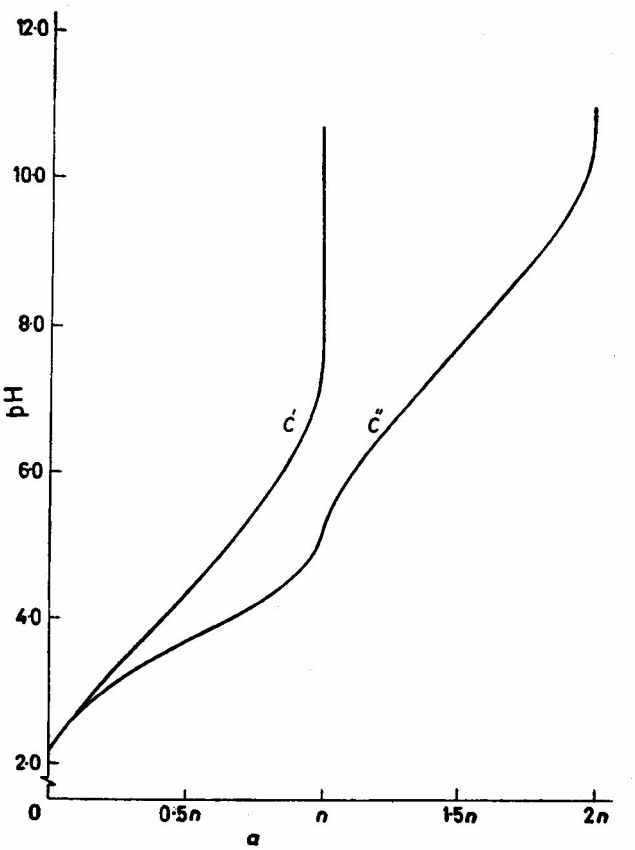

Fig. 3 — Titration curves for the complexes (MA and MA_2) — moles of alkali used per mole of metal ion (a) vs pH [Curve C': MA; curve C'': MA_2]

by Chaberek and Martell[5] may then be plotted. These curves can be utilized to explain the reaction equilibria of the proton dissociation and the metal-chelate formation, and the equilibrium constants can be evaluated as discussed in the following account.

Calculations

(1) *Proton dissociation constants* — the proton dissociation constants K^H_{1A}, K^H_{2A}, ... K^H_{nA} for the ligand H_nA which dissociates as under:

$$H_nA \rightleftharpoons H_{n-1}A^- + H^+; \; K^H_{1A} = \frac{[H_{n-1}A^-][H^+]}{[H_nA]} \quad ...(1a)$$

$$H_{n-1}A^- \rightleftharpoons H_{n-2}A^{2-} + H^+; \; K^H_{2A} = \frac{[H_{n-2}A^{2-}][H^+]}{[H_{n-1}A^-]} \quad ...(1b)$$

$$HA^{(n-1)-} \rightleftharpoons A^{n-} + H^+; \; K^H_{nA} = \frac{[A^{n-}][H^+]}{[HA^{(n-1)-}]} \quad ...(1n)$$

can be calculated using the a vs pH curve. The total [ligand] which can be obtained using the initial concentration and the total volume at each pH, is given by Eq. (2)

$$C_A = [H_nA] + [H_{n-1}A^-] + [H_{n-2}A^{2-}] + \ldots + [A^{n-}] \quad ...(2)$$

Applying mass and charge balance relations

$$aC_A = [H_{n-1}A^-] + 2[H_{n-2}A^{2-}] + \ldots + n[A^{n-}] \quad ...(3)$$

From Eqs. (2) and (3):

$$C_A(n-a) = n[H_nA] + (n-1)[H_{n-1}A^-] + (n-2)[H_{n-2}A^{2-}] + \ldots + [HA^{(n-1)-}] \quad ...(4)$$

Thus the dissociation constants can be evaluated considering the pH and Bjerrum's function, average number of protons attached per ligand ($\bar{n}_A$), which is given by:

$$\bar{n}_A = \frac{n[H_nA] + (n-1)[H_{n-1}A^-] + (n-2)[H_{n-2}A^{2-}] + \ldots + [HA^{(n-1)-}]}{C_A} = (n-a) \quad ...(5)$$

If the curve in Fig. 2 does not show prominent inflections, then each point has to be considered for calculating the values of the dissociation constants. On the other hand, if the proton dissociation of the functional groups takes place in steps showing sharp inflections, the calculation is simplified. Thus, for the dissociation of the first two protons of H_nA which shows sharp inflections at $a=1$ and 2, $C_A = [H_nA] + [H_{n-1}A^-]$, $aC_A = [H_{n-1}A^-]$ between $a=0$ and 1; and $C_A = [H_{n-1}A^-] + [H_{n-2}A^{2-}]$, $aC_A = [H_{n-1}A^-] + 2[H_{n-2}A^{2-}]$ between $a=1$ and 2, ignoring the existence of the other species. Therefore the values of K^H_{1A} and K^H_{2A} are $a[H^+]/(1-a)$ and $(a-1)[H^+]/(2-a)$, respectively.

(2) *Simple chelate species of the type MA_n* — the metal ion M^{z+} [employed as $M(ClO_4)_z$] with H_nA may form various non-protonated chelate species like $MA^{(n-z)-}$, $MA_2^{(2n-z)-}$, ... $M_2A^{(n-2z)-}$, etc. The present method of calculation is similar to that of the algebraic method[5] and the calculations for the 1:1 and 1:2 metal-ligand species only are given here.

The titration curves, plotted between a (moles of alkali per mole of metal ion) and pH for reactions between M^{z+} and H_nA, consists of inflections at $a=n$ and $2n$ respectively (Fig. 3) for 1:1 (curve C') and 1:2 (curve C'') metal to ligand ratios. The formation constants

$$K_{1A} = \frac{[MA^{(n-z)-}]}{[M^{z+}][A^{n-}]} \text{ and } K_{2A} = \frac{[MA_2^{(2n-z)-}]}{[MA^{(n-z)-}][A^{n-}]}$$

may be evaluated after calculating the values of $[M^{z+}]$, $[A^{n-}]$, $[MA^{(n-z)-}]$ and $[MA_2^{(2n-z)-}]$. Thus for the titration of 1:1 metal to ligand ratios

$$C_A = [H_nA]+[H_{n-1}A^-] +[H_{n-2}A^{2-}]+ \ldots +[A^{n-}]+[MA^{(n-z)-}] \quad \ldots(6)$$

$$C_M = [M^{z+}]+[MA^{(n-z)-}] \quad \ldots(7)$$

$[M^{z+}]$ is the concentration of uncomplexed metal ion

$$aC_A = [H_{n-1}A^-]+2[H_{n-2}A^{2-}]+ \ldots +n[A^{n-}] +n[MA^{(n-z)-}] \quad \ldots(8)$$

Introducing the dissociation constants of the ligand and substituting the value of $[MA^{(n-z)-}]$ from Eq. (6) into Eq. (18) we get

$$[A^{n-}] = \frac{(n-a)C_A}{\frac{[H^+]^n}{K^H_{1A}K^H_{2A}\ldots K^H_{nA}}+\frac{[H^+]^{n-1}}{K^H_{2A}K^H_{3A}\ldots K^H_{nA}}+\ldots+\frac{[H^+]}{K^H_{nA}}} \quad \ldots(9)$$

Therefore,

$$[MA^{(n-z)-}] = C_A - Y_1[A^{n-}] \quad \ldots(10)$$

$$[M^{z+}] = Y_1[A^{n-}] \quad \ldots(11)$$

where

$$Y_1 = \frac{[H^+]^n}{K^H_{1A}K^H_{2A}K^H_{3A}\ldots K^H_{nA}}+\frac{[H^+]^{n-1}}{K^H_{2A}K^H_{3A}\ldots K^H_{nA}}+\ldots+\frac{[H^+]}{K^H_{nA}}+1 \quad \ldots(12)$$

When inflection occurs at $a=2n$ for 1:2 metal to ligand reaction:

$$C_M = [M^{z+}]+[MA^{(n-z)-}]+[MA_2^{(2n-z)-}] \quad \ldots(13)$$

$$C_A = [H_nA]+[H_{n-1}A^-]+[H_{n-2}A^{2-}]+\ldots+[A^{n-}] +[MA^{(n-z)-}]+2[MA_2^{(2n-z)-}] \quad \ldots(14)$$

and

$$aC_M = [H_{n-1}A^-]+2[H_{n-2}A^{2-}]+\ldots+n[A^{n-}] +n[MA^{(n-z)-}]+2n[MA_2^{(2n-z)-}] \quad \ldots(15)$$

or

$$aC_A = 2[H_{n-1}A^-]+4[H_{n-2}A^{2-}]+\ldots+2n[A^{n-}]+ 2n[MA^{(n-z)-}]+4n[MA_2^{(2n-z)-}] \quad \ldots(16)$$

From Eqs. (14) and (16):

$$C_A(2n-a) = 2n[H_nA]+(2n-2)[H_{n-1}A^-]+ (2n-4)[H_{n-2}A^{2-}]+\ldots+2[A^{n-}] \quad \ldots(17)$$

or

$$[A^{n-}] = \frac{C_A(2n-a)}{\left(\frac{2n[H^+]^n}{K^H_{1A}K^H_{2A}K^H_{3A}\ldots K^H_{nA}}+\frac{(2n-2)[H^+]^{n-1}}{K^H_{2A}K^H_{3A}\ldots K^H_{nA}}+\ldots+\frac{2[H^+]}{K^H_{nA}}\right)} \quad \ldots(18)$$

K_{1A} and K_{2A} can be calculated considering the Bjerrum quantity $\bar{n}$ and pL. The following expression for $\bar{n}$ can be derived using Eqs. (14) and (18):

$$\bar{n} = \frac{[MA^{(n-z)-}]+2[MA_2^{(2n-z)-}]}{C_M} = \frac{C_A - Y_1[A^{n-}]}{C_M} \quad \ldots(19)$$

K_{2A} can also be evaluated from $[M^{z+}]$, $[MA_2^{(2n-z)-}]$, $[A^{n-}]$ and introducing the K_{1A} value. Thus from Eqs. (13) and (14):

$$[M^{z+}] = \frac{Y_1[A^{n-}]}{2+K_{1A}[A^{n-}]} \quad \ldots(20)$$

Similarly from Eqs. (13) and (20)

$$[MA_2^{(2n-z)-}] = C_M - \frac{Y_1[A^{n-}](1+K_{1A}[A^{n-}])}{2+K_{1A}[A^{n-}]} \quad \ldots(21)$$

(3) *Protonated and hydroxo complexes* — If in the metal-ligand reactions some protons of the fuctional groups of the ligand remain undissociated even after complexation, protonated complex species result. Therefore polydentate ligands only may be considered for the investigation of such reactions. Schwarzenbach[9-11] developed a potentiometric method for the investigation of such systems carrying out the experiments in the presence of a large excess of metal ions. The method can be applied for complexes which have more than three protons. If, however, the titration mixtures do not contain an excess of free acid[12], low pH values are not attained and information cannot be obtained for all the protonated species. The method of Beck and Görög[13,14] can be used with fairly acidic solutions, assuming that the concentration of free metal ion or the sum of the concentrations of the complexes can be determined. Österberg[15,16] also considered general equilibria involving protonation.

In the present treatment, the basis of approach is the algebraic method. The charges on the ions are omitted for the sake of simplicity. Considering the 1:1 (metal to ligand) interaction between M and H_nA forming the protonated species MH_xA showing inflection at $a=(n-x)$, the equilibria for the formation of MH_xA and the dissociation of its protons are:

$$M+H_xA \rightleftharpoons MH_xA;\ K'_A = \frac{[MH_xA]}{[M][H_xA]} \quad \ldots(22a)$$

$$MH_xA \rightleftharpoons MH_{x-1}+H^+;\ K^{H'}_{1A} = \frac{[MH_{x-1}A][H^+]}{[MH_xA]} \quad \ldots(22b)$$

$$MH_{x-1}A \rightleftharpoons MH_{x-2}A+H^+;\ K^{H'}_{2A} = \frac{[MH_{x-2}A][H^+]}{[MH_{x-1}A]} \quad \ldots(22c)$$

$$MHA \rightleftharpoons MA+H^+;\ K^{H'}_{xA} = \frac{[MA][H^+]}{[MHA]} \quad \ldots(22x)$$

The stability constant K'_A can be evaluated similar to 1:1 species ignoring the existence of other species which are obtained after proton dissociation from MH_xA. Further, assuming the whole of the metal ions and the ligands to be consumed in the formation of (MH_xA) species, the equilibria (22b), (22c) ... (22x) can be treated as proton dissociation of the ligand and the values of the dissociation constants, $K^{H'}_{A1}$, $K^{H'}_{2A}$, ..., $K^{H'}_{xA}$ can be evaluated.

Considering the charges of $H_{x-1}A^{(n+1-x)-}$, $H_{x-2}A^{(n+2-x)-}$, ..., A^{n-}, it appears that the free [metal ion] and the free [ligand] will decrease and [MA] will increase. But these changes will depend

upon the stability constant of MH_xA. Hence in cases where $a > (n-x)$ the following equilibria will also exist:

$$M+H_{x-1}A \rightleftharpoons MH_{x-1}A;\ K'_{1A} = \frac{[MH_{x-1}A]}{[M][H_{x-1}A]} \quad ...(23a)$$

$$M+H_{x-2}A \rightleftharpoons MH_{x-2}A;\ K'_{2A} = \frac{[MH_{x-2}A]}{[M][H_{x-2}A]} \quad ...(23b)$$

$$M+A \rightleftharpoons MA;\ K'_{xA} = \frac{[MA]}{[M][A]} \quad ...(23x)$$

For the high value of K'_A (i.e. maximum association of M ion in the complex) the validity of the assumption $C_M = C_A = [MH_xA]$ will not be much affected and the values of $K'_{1A}, K'_{2A}, \ldots, K'_{xA}$ can be evaluated from the following relations introducing the values of complex dissociation constants. When the value of a is between $(n-x)$ and $(n+1-x)$

$$C_M = [M]+[MH_xA]+[MH_{x-1}A] \quad ...(24)$$

$$C_A = [H_nA]+[H_{n-1}A]+\ldots+[H_{x-1}A]+[MH_xA]+[MH_{x-1}A] \quad ...(25)$$

The following is obtained by mass and charge balance relation [vide Eqs. (3) and (8)]

$$aC_A = [H_{n-1}A]+2[H_{n-2}A]+\ldots+(n+1-x)[H_{x-1}A]+(n-x)[MH_xA]+(n+1-x)[MH_{x-1}A] \quad ...(26)$$

From Eq. (25):

$$C_A = Y_2[H_{x-1}A]+[MH_{x-1}A]\left(1+\frac{[H^+]}{K^{H'}_{1A}}\right) \quad ...(27)$$

where

$$Y_2 = \frac{[H^+]^{(n+1-x)}}{K^H_{1A}K^H_{2A}K^H_{3A}\ldots K^H_{(n+1-x)A}} + \frac{[H^+]^{(n-x)}}{K^H_{2A}K^H_{3A}\ldots K^H_{(n+1-x)A}} + \ldots + \frac{[H^+]}{K^H_{(n+1-x)A}} + 1 \quad ...(28)$$

$$[MH_{x-1}A] = \frac{C_A - Y_2[H_{x-1}A]}{\left(1+\frac{[H^+]}{K^{H'}_{1A}}\right)} \quad ...(29)$$

Similarly from Eq. (26)

$$aC_A = Y_3[H_{x-1}A] + [MH_{x-1}A]\times\left(n+1-x+\frac{(n-x)[H^+]}{K^{H'}_{1A}}\right) \quad ...(30)$$

where

$$Y_3 = \frac{[H^+]^{(n-x)}}{K^H_{2A}K^H_{3A}K^H_{4A}\ldots K^H_{(n+1-x)A}} + \frac{2[H^+]^{(n-x-1)}}{K^H_{3A}K^H_{4A}\ldots K^H_{(n+1-x)A}} + \ldots + \frac{(n-x)[H^+]}{K^H_{(n+1-x)A}} + (n+1-x) \quad ...(31)$$

Substituting $[MH_{x-1}A]$ from equation (29)

$$aC_A = Y_3[H_{x-1}A] + \frac{(C_A - Y_2[H_{x-1}A])}{\left(1+\frac{[H^+]}{K^{H'}_{1A}}\right)} \times \left(n+1-x+\frac{(n-x)[H^+]}{K^{H'}_{1A}}\right) \quad ...(32)$$

$$\text{or } [H_{x-1}A] = \frac{C_A(a-r)}{(Y_3 - Y_2 r)} \quad ...(33)$$

$$\text{where } r = \frac{(n+1-x)+\frac{(n-x)[H^+]}{K^{H'}_{1A}}}{\left(1+\frac{H^+}{K^{H'}_{1A}}\right)} \quad ...(34)$$

From Eqs. (24), (25) and (28)

$$[M] = Y_2[H_{x-1}A] \quad ...(35)$$

Thus the values of $[H_{x-1}A]$, $[MH_{x-1}A]$, [M] obtained from Eqs. (33), (29) and (35) respectively can be used for the determination of K'_{1A}. But the value of K'_{1A} may vary near $a=(n+1-x)$ due to the formation of $MH_{x-2}A$ in small amounts, may be neglected. $K'_{2A}, K'_{3A}, \ldots, K'_{xA}$ can also be determined by a similar treatment. A likewise approach can be made for 1:0·5, 1:2, 1:3 etc metal to ligand complex species. When $C_M = C_A \neq [MH_xA]$, value of $K^{H'}_{1A}$ will be approximate, which cannot be used for the determination of $[H_{x-1}A]$.

Alternatively, $K^{H'}_{1A}$ and K'_{1A} can be evaluated considering the formation constant K'_A as under:

$$C_M = [M]+[MH_xA]+[MH_{x-1}A] \quad ...(36)$$

$$C_A = [H_nA]+[H_{n-1}A]+[H_{n-2}A]+\ldots+[H_{x-1}A]+[MH_xA]+[MH_{x-1}A] \quad ...(37)$$

$$aC_A = [H_{n-1}A]+2[H_{n-2}A]+\ldots+(n+1-x)[H_{x-1}A]+(n-x)[MH_xA]+(n+1-x)[MH_{x-1}A] \quad ...(38)$$

Substituting the value of $[MH_{x-1}A]$ from equation (37) in equation (38)

$$C_A(n+1-x-a) = (n+1-x)[H_nA]^2+(n-x)[H_{n-1}A]+\ldots+[H_xA]+[MH_xA] = Y_4[H_{x-1}A]+\frac{K'_A[M][H_{x-1}A][H^+]}{K^H_{(n+1-x)A}} \quad ...(39)$$

Replacing [M] by $Y_2[H_{x-1}A]$:

$$C_A(n+1-x-a) = Y_4(H_{x-1}A]+\frac{K'_A Y_2[H_{x-1}A]^2\,[H^+]}{K^H_{(n+1-x)A}} \quad ...(40)$$

where

$$Y_4 = \frac{(n+1-x)[H^+]^{(n+1-x)}}{K^H_{1A}K^H_{2A}K^H_{3A}\ldots K^H_{(n+1-x)A}} + \frac{(n-x)[H^+]^{(n-x)}}{K^H_{2A}\ldots K^H_{(n+1-x)A}} + \ldots + \frac{[H^+]}{K^H_{(n+1-x)A}} \quad ...(41)$$

Substituting the value of [M] and $[MH_xA]$ in Eq. (36)

$$[MH_{x-1}A] = C_M - Y_2[H_{x-1}A] - \frac{K'_A Y_2[H^+][H_{x-1}A]^2}{K^H_{(n+1-x)A}} \quad ...(42)$$

Thus correct value of K'_{1A} can be calculated using Eqs. (35) and (40-42). $K^{H'}_{1A}$ can also be calculated accurately using $[MH_xA]$, $[MH_{x-1}A]$ and pH.

Also, since the solubility product $[M][OH]^z$ is a very small quantity for most of the coordinating metal ions, [M] should decrease or the association of metal ions with ligand should increase (it is possible only for protonated metal complexes as above) to keep the reaction mixture in solution. Where this condition of association of metal ion is not followed and [M] is in excess the complex breaks up and the whole of the metal ion is converted into an insoluble hydroxide. At higher pH (or from the pH of the association of OH^- with the metal), [M] will decrease appreciably due to the formation of metal hydroxo species, and $M:A \gg 1$, leading to favourable condition for the formation of MA_2

species. If MA is stable the change in [MA] will be negligible inspite of metal and OH^- association; and $[MA_2]$ would also be negligible. Further, in cases where more than one ligand cannot be attached to the metal ion, no other species except the metal hydroxo species and MA would exist. If the protonated species are formed in the *p*H range where metal hydroxo species exist both of these should be taken into consideration. From ac onsideration of mononuclear metal hydroxy species in Eqs. (36) and (39) respectively the following equations are obtained:

$$C_M=[M]+[MH_xA]+[MH_{x-1}A]+[M(OH]+[M(OH)_2]+\ldots+[M(OH)_z] \quad \ldots(43)$$

$$C_A(n+1-x-a)=(n+1-x)[H_nA]+(n-x)[H_{n-1}A]+\ldots+[H_xA]+[MH_xA]-[M(OH)]-[M(OH)_2]-\ldots-[M(OH)_z] \quad \ldots(44)$$

From Eqs. (37) and (43)

$$[M]=\frac{Y_2[H_{x-1}A]}{(1+K_1[OH^-]+K_1K_2[OH^-]^2+\cdots+K_1K_2\ldots K_z[OH^-]^z)} \quad \ldots(45)$$

$$C_A(n+1-x-a)=Y_4[H_{x-1}A]+\frac{K'_AY_2[H^+][H]_{x-1}A]^2}{Y_5K^H_{(n+1-x)A}}-\frac{Y_2Y_6[H_{x-1}A]}{Y_5} \quad \ldots(46)$$

where

$$Y_5=1+K_1[OH^-]+K_1K_2[OH^-]^2+\ldots+K_1K_2\ldots K_z[OH^-]^z \quad \ldots(47)$$

$$Y_6=K_1[OH^-]+2K_1K_2[OH^-]^2+\ldots+zK_1K_2\ldots K_z[OH^-]^z \quad \ldots(48)$$

Therefore,

$$C_A(n+1-x-a)=[H_{x-1}A]\left(Y_4-\frac{Y_2Y_6}{Y_5}\right)+[H_{x-1}A]^2\left(\frac{K'_AY_2[H^+]}{Y_5K^H_{(n+1-x)A}}\right) \quad \ldots(49)$$

Eq. (49) can be used for the determination of $[H_{x-1}A]$. Similarly from Eqs. (43) and (45):

$$[MH_xA]+[MH_{x-1}A]=C_M-\frac{Y_2[H_{x-1}A]}{Y_5} \quad \ldots(50)$$

or

$$[MH_{x-1}A]=C_M-\frac{Y_2[H_{x-1}A]}{Y_5}\left(1+\frac{K'_A[H^+][H_{x-1}A]}{K^H_{(n+1-x)A}}\right) \quad \ldots(51)$$

Similar calculations can be employed for the determination of K'_{2A}, K'_{3A}, ..., K'_{xA}.

When the complexes are highly stable (C_M or C_A is assumed to be involved in the complex species) the increase in the values of *a* after $a=n$ will indicate the formation of hydroxo complexes involving the undermentioned equilibria:

$$MA+OH^-\rightleftharpoons M(OH)A,\ K'_1=\frac{[M(OH)A]}{[MA][OH^-]} \quad \ldots(52a)$$

$$M(OH)A+OH\rightleftharpoons M(OH)_2A;\ K'_2=\frac{[M(OH)_2A]}{[M(OH)A][OH^-]} \quad \ldots(52b)$$

$$M(OH)_{i-1}A+OH^-\rightleftharpoons M(OH);A,K'_i=\frac{[M(OH)A_i]}{[M(OH)_{i-1}A][OH^-]} \quad \ldots(52i)$$

$$C_M=C_A=[MA]+[M(OH)A]+[M(OH)_2A]+\ldots+[M(OH)_iA] \quad \ldots(53)$$

$$aC_A=n[MA]+(n+1)[M(OH)A]+(n+2)[M(OH)_2A]+\ldots+(n+i)[M(OH)_iA] \quad \ldots(54)$$

$$\text{or } C_A(a-n)=[M(OH)A]+2[M(OH)_2A]+\ldots+i[M(OH)_iA] \quad \ldots(55)$$

Hence

$$\bar{n}_{OH}=\frac{[M(OH)A]+2[M(OH)_2A]+\ldots+i[M(OH)_iA]}{[MA]+[M(OH)A]+[M(OH)_2A]+\ldots+[M(OH)_iA]}=\frac{C_A(a-n)}{C_A}=(a-n) \quad \ldots(56)$$

Values of $(a-n)$ and *p*OH values can be used for the determination of the constants.

Further, where consecutive reactions of the type indicated below take place:

$$M+A+OH^-\rightleftharpoons M(OH)A;\ K''_1=\frac{[M(OH)A]}{[M][A][OH^-]} \quad \ldots(57a)$$

$$M+A+2(OH^-)\rightleftharpoons M(OH)_2A;\ K''_2=\frac{[M(OH)_2A]}{[M][A][OH^-]^2} \quad \ldots(57b)$$

$$M+A+i(OH^-)\rightleftharpoons M(OH)_iA;\ K''_i=\frac{[M(OH)_iA]}{[M][A][OH^-]^i} \quad \ldots(57)$$

the formation constants can be evaluated introducing the concentration of metal hydroxo species and then adopting method as used in the protonated systems. Thus when $a=n$ and $(n+1)$

$$C_M=[M]+[MH_xA]+[MH_{x-1}A]+\ldots+[MA]+[M(OH)A]+[M(OH)]+[M(OH)_2]+\ldots+[M(OH)_z] \quad \ldots(58)$$

$$C_A=[H_nA]+[H_{n-1}A]+\ldots+[A]+[MH_xA]+[MH_{x-1}A]+\ldots+[MA]+[M(OH]A] \quad \ldots(59)$$

$$aC_A=[H_{n-1}A]+2[H_{n-2}A]+\ldots+n[A]+(n-x)[MH_xA]+(n+1-x)[MH_{x-1}A]+\ldots+n[MA]+(n+1)[M(OH)A]+[M(OH)]+2[M(OH)_2]+\ldots+i[M(OH)_i] \quad \ldots(60)$$

$$C_A(n+1-a)=(n+1)[H_nA]+n[H_{n-1}A]+\ldots+[A]+(x+1)[MH_xA]+x[MH_{x-1}A]+\ldots+[MA]-[M(OH)]-2[M(OH)_2]-\ldots-\theta z[M(OH)_z]=(n+1)Y_7[A]+[M][A]Y_8-[M]Y_6 \quad \ldots(61)$$

where

$$Y_7=\frac{(n+1)[H^+]^n}{K^H_{1A}K^H_{2A}\ldots K^H_{nA}}+\frac{n[H^+]^{n-1}}{K^H_{2A}\ldots K^H_{nA}}+\ldots+\frac{2[H^+]}{K^H_{nA}}+1 \quad \ldots(62)$$

$$Y_8=\frac{(x+1)K'_A[H^+]^x}{K^H_{(n+1-x)A}K^H_{(n+2-x)A}\ldots K^H_{nA}}+\frac{xK'_{1A}[H^+]^{x-1}}{K^H_{(n+2-x)A}\ldots K^H_{nA}}+\ldots+\frac{2[H^+]}{K^H_{nA}}+1 \quad \ldots(63)$$

But $[M]=\frac{Y_9[A]}{Y_5}$ from equations (58) and (59)

where

$$Y_9=Y_1=\frac{[H^+]^n}{K^H_{1A}K^H_{2A}\ldots K^H_{nA}}+\frac{[H^+]^{n-1}}{K^H_{2A}\ldots K^H_{nA}}+\ldots+\frac{[H^+]}{K^H_{nA}}+1 \quad \ldots(64)$$

Therefore,

$$C_A(n+1-a)=\left(Y_7(n+1)-\frac{Y_9Y_6}{Y_5}\right)[A]+\frac{Y_8Y_9}{Y_5}[A]^2 \quad \ldots(65)$$

The value of [A] obtained from Eq. (65) can be used for the determination of [M]. [M(OH)A] can be calculated from Eq. (59) introducing the values of [M] and [A].

(4) *Mixed ligand complexes* — Two types of mixed ligand complexes are formed in solution, depending upon the affinity of the ligands A and B involved. In the first type MA is more stable than MB and ligand exchange does not occur between MA and B (where A and B are recognized respectively as primary and secondary ligands)[17-19].

The second type is more complicated, where the affinity of the two ligands is comparable, and both A and B may combine with M simultaneously. A number of mathematical approaches have been made to calculate the stability constants in such systems[20-29].

In view of the inherent limitations of the methods, it was considered useful to extend the approach described in this paper to mixed ligand systems involving two or more ligands. Moreover, equilibria involving more than two ligands, e.g. MABC, MABCD, etc., have not received proper attention. Here, a method of calculation of a general nature has been described which can profitably be employed even in cases of metal ions of high coordination numbers combining with polydentate ligands of comparable metal binding affinity.

(*i*) *Systems involving two ligands* — If M reacts with H_nA and H_lB separately to form 1:1 and 1:2 (metal: ligand) complexes in each case, the formation of MAB would occur if equal amounts of M, H_nA, and H_lB are mixed together. The presence of MAB can be inferred from (*i*) the titration curve (pH vs a) of the mixed system (where a is the moles of alkali used per mole of ligand), which would show an inflection at $a=(n+l)$, and (*ii*) by comparing with the titration curves of 1:1 and 1:2 species of both the ligands.

In the solution in addition to the equilibria (1a), (1b)...(1n), the following equilibria would be expected to exist:

$$H_lB \rightleftharpoons H_{l-1}B + H^+;\ K^H_{1B} = \frac{[H_{l-1}B][H^+]}{[H_lB]} \quad ...(66a)$$

$$H_{l-1}B \rightleftharpoons H_{1-2}B + H^+;\ K^H_{2B} = \frac{[H_{l-2}B][H^+]}{[H_{l-1}B]} \quad ...(66b)$$

$$HB \rightleftharpoons B + H^+;\ K^H_{lB} = \frac{[B][H^+]}{[HB]} \quad ...(66l)$$

$$M + A \rightleftharpoons MA;\ K_{1A} = \frac{[MA]}{[M][A]} \quad ...(67)$$

$$MA + A \rightleftharpoons MA_2;\ K_{2A} = \frac{[MA_2]}{[MA][A]} \quad ...(68)$$

$$M + B \rightleftharpoons MB;\ K_{1B} = \frac{[MB]}{[M][B]} \quad ...(69)$$

$$MB + B \rightleftharpoons MB_2;\ K_{2B} = \frac{[MB_2]}{[MB][B]} \quad ...(70)$$

$$M + A + B \rightleftharpoons MAB;\ K = \frac{[MAB]}{[M][A][B]} \quad ...(71)$$

Hence

$$C_M = [M]+[MA]+[MA_2]+[MB]+[MB_2]+[MAB] \quad ...(72)$$

$$C_A = [H_nA]+[H_{n-1}A]+\cdots+[A]+[MA]+2[MA_2]+[MAB] \quad ...(73)$$

$$C_B = [H_lB]+[H_{l-1}B]+\cdots+[B]+[MB]+2[MB_2]+[MAB] \quad ...(74)$$

$$aC_M = [H_{n-1}A]+2[H_{n-2}A]+\cdots+n[A]+[H_{l-1}B]+2[H_{l-2}B]+\cdots+l[B]+n[MA]+2n[MA_2]+l[MB]+2l[MB_2]+(n+l)[MAB] \quad ...(75)$$

From Eqs. (73)-(75)

$$aC_M = nC_A + lC_B - (n[H_nA]+(n-1)[H_{n-1}A]+\cdots+[HA]+l[H_lB]+[l-1][H_{l-1}B]+\cdots+[HB]) \quad ...(76)$$

or $$C_M(n+l-a) = a_1[A]+b_1[B] \quad ...(77)$$

where

$$a_1 = \frac{n[H^+]^n}{K^H_{1A}K^H_{2A}\cdots K^H_{nA}} + \frac{(n-1)[H^+]^{(n-1)}}{K^H_{2A}K^H_{3A}\cdots K^H_{nA}} + \cdots + \frac{[H^+]}{K^H_{nA}} \quad ...(78)$$

$$b_1 = \frac{l[H^+]^l}{K^H_{1B}K^H_{2B}\cdots K^H_{lB}} + \frac{(l-1)[H^+]^{(l-1)}}{K^H_{2B}K^H_{3B}\cdots K^H_{lB}} + \cdots + \frac{[H^+]}{K^H_{lB}} \quad ...(79)$$

Further

$$C_M - C_A = [M]+[MB]+[MB_2]-[MA_2] - ([H_nA]+[H_{n-1}A]+\cdots+[A]) \quad ...(80)$$

$$C_M - C_B = [M]+[MA]+[MA_2]-[MB_2]-([H_lB] + [H_{l-1}B]+\cdots+[B]) \quad ...(81)$$

Introducing the dissociation constants of the ligand and the stability constants of the mononuclear metal-ligand complexes [from Eqs. (1), (66)-(70)], Eqs. (80) and (81) respectively can be written as:

$$[M](1+K_{1B}[B]+K_{1B}K_{2B}[B]^2-K_{1A}K_{2A}[A]^2) = a_2[A] \quad ...(82)$$

$$[M](1+K_{1A}[A]+K_{1A}K_{2A}[A]^2-K_{1B}K_{2B}[B]^2) = b_2[B] \quad ...(83)$$

where

$$a_2 = \frac{[H^+]^n}{K^H_{1A}K^H_{2A}\cdots K^H_{nA}} + \frac{[H^+]^{(n-1)}}{K^H_{2A}K^H_{3A}\cdots K^H_{nA}} + \cdots + \frac{[H^+]}{K^H_{nA}} + 1 \quad ...(84)$$

$$b_2 = \frac{[H^+]^l}{K^H_{1B}K^H_{2B}\cdots K^H_{lB}} + \frac{[H^+]^{(l-1)}}{K^H_{2B}K^H_{3B}\cdots K^H_{lB}} + \cdots + \frac{[H^+]}{K^H_{lB}} + 1 \quad ...(85)$$

Combination of the Eqs. (82), (83) gives:

$$[M] = \frac{a_2[A]}{1+K_{1B}[B]+K_{1B}K_{2B}[B]^2-K_{1A}K_{2A}[A]^2} \quad ...(86)$$

$$= \frac{b^2[B]}{1+K_{1A}[A]+K_{1A}K_{2A}[A]^2-K_{1B}K_{2B}[B]^2} \quad ...(87)$$

From Eq. (77)

$$[B] = e_1 - d[A] \quad ...(88)$$

where $e_1 = \frac{C_M(n+l-a)}{b_1}$, $d = \frac{a_1}{b_1}$

Substituting the value of [B] in Eqs. (86) and (87)

$$P_1[A]^3+P_2[A]^2+P_3[A]-P_4 = 0 \quad ...(89)$$

where

$$P_1 = K_{1A}K_{2A}(a_2-b_2d)+K_{1B}K_{2B}(b_2d^3-a_2d^2) \quad ...(90)$$

$$P_2 = K_{1B}K_{2B}(2a_2e_1d-3b_2e_1d^2)+K_{1A}K_{2A}b_2e_1 + a_2K_{1A}-d^2b_2K_{1B} \quad ...(91)$$

$$P_3 = K_{1B}K_{2B}(3b_2de_1^2-a_2^2e_1^2)+2K_{1B}db_2e_1+a_2+b_2d \quad ...(92)$$

$$P_4 = b_2e_1+K_{1B}b_2e_1^2+b_2e_1^3K_{1B}K_{2B} \quad ...(93)$$

Eq. (89) will give the value of [A], which on substitution in Eq. (88), would give [B]. Now utilizing [A] and [B], [M] can be determined from Eq. (86) or (87). [MAB] can be calculated considering [M], [A], [B] and the stability constants of the mononuclear systems. If one of the ligands H_nA or H_lB has a tendency to form only 1:1 mononuclear complex the calculation for the mixed complex would be easy.

(ii) Systems involving three ligand molecules (Two different ligands only) — If M is capable of forming MA_3 and MB_3, there will also be possibility of the formation of MA_2B and MAB_2. The following equilibria can be considered from the 1:2:1 or 1:1:2 mixture of M:A:B in addition to the equilibria (1), (66)-(71). In a 1:2:1 mixture

$$MA_2+A \rightleftharpoons MA_3;\ K_{3A}=\frac{[MA_3]}{[MA_2][A]} \quad ...(94)$$

$$MB_2+B \rightleftharpoons MB_3;\ K_{3B}=\frac{[MB_3]}{[MB_2][B]} \quad ...(95)$$

$$M+2A+B \rightleftharpoons MA_2B;\ K_{2A1B}=\frac{[MA_2B]}{[M][A]^2[B]} \quad ...(96)$$

Here, the existence of the species 1:1:2 can be ignored*.

$$C_M=[M]+[MA]+[MA_2]+[MA_3]+[MB]+[MB_2]+[MB_3]+[MAB]+[MA_2B] \quad ...(97)$$

$$C_A=[H_nA]+[H_{n-1}A]+\cdots+[A]+[MA]+2[MA_2]+3[MA_3]+[MAB]+2[MA_2B] \quad ...(98)$$

$$C_B=[H_lB]+[H_{l-1}B]+\cdots+[B]+[MB]+2[MB_2]+3[MB_3]+[MAB]+[MA_2B] \quad ...(99)$$

$$aC_M=[H_{n-1}A]+2[H_{n-2}A]+\cdots+n[A]+n[MA]+2n[MA_2]+3n[MA_3]+[H_{l-1}B]+2[H_{l-2}B]+\cdots+l[B]+l[MB]+2l[MB_2]+3l[MB_3]+(n+l)[MAB]+(2n+l)[MA_2B] \quad ...(100)$$

or $C_M(2n+l-a)=a_1[A]+b_1[B]$

or $[B]=e_2-d[A]$ ...(101)

where $e_2=\dfrac{C_M(2n+l-a)}{b_1}$.

Further changing Eqs. (97)-(99) into $2C_M-C_A$ and C_M-C_B the following is obtained:

$$[M]=a_2[A]/(2+K_{1A}[A]-K_{1A}K_{2A}K_{3A}[A]^3+K[A][B]+2K_{1B}[B]+2K_{1B}K_{2B}[B]^2+2K_{1B}K_{2B}K_{3B}[B]^3)=b_2[B]/(1+K_{1A}[A]+K_{1A}K_{2A}[A]^2+K_{1A}K_{2A}K_{3A}\times[A]^3-K_{1B}K_{2B}[B]^2-2K_{1B}K_{2B}K_{3B}[B]^3) \quad ...(102)$$

Substituting [B] from Eq. (101) the equation for [A] can be obtained in the following form:

$$T_1[A]^4+T_2[A]^3+T_3[A]^2+T_4[A]-T_5=0 \quad ...(103)$$

where

$$T_1=K_{1A}K_{2A}K_{3A}(a_2-b_2d)+2K_{1B}K_{2B}K_{3B}(a_2d^3-b_2d^4) \quad ...(104)$$

$$T_2=K_{1A}K_{2A}(a_2+b_2e_2K_{3A})+K_{1B}K_{2B}K_{3B}\times(8b_2e_2d^3-6a_2e_2^2d)+K_{1B}K_{2B}(2b_2d^3-a_2d^2)-b_2d^2K \quad ...(105)$$

$$T_3=K_{1B}K_{2B}K_{3B}(6a_2e_2^2d-12b_2d^2e_2^2)+K_{1B}K_{2B}(2a_2e_2d-6b_2e_2d^2)+K_{1A}(a_2+2b_2d)+b_2e_2dK-2K_{1B}b_2d^2 \quad ...(106)$$

$$T_4=K_{1B}K_{2B}K_{3B}(8b_2de_2^3-2a_2e_2^3)+K_{1B}K_{2B}(4b_2e_2^2d+2b_2de_2^3-a_2e_2^3)+4K_{1B}b_2e_2d+2b_2d+a_2-b_2e_2^2K-b_2e_2K_{1A} \quad ...(107)$$

$$T_5=2b_2e_2(1+e_2K_{1B}+e_2^2K_{1B}K_{2B}+e_2^3K_{1B}K_{2B}K_{3B}) \quad ...(108)$$

Thus [A], [B], [M], $[MA_2B]$ can be determined.

Similarly with a 1:1:2 mixture the stability constant $K_{1A2B}=\dfrac{[MAB_2]}{[M][A][B]^2}$ can be evaluated.

(iii) *Systems involving three different ligands* — If three different ligands H_nA, H_lB and H_mC are involved in a mixture of 1:1:1:1 (M:H_nA:H_lB: H_mC) the equilibria (1), (66)-(71), (94)-(96) and (109)-(120) can be considered.

$$H_mC \rightleftharpoons H_{m-1}C+H^+;\ K_{1C}^H=\frac{[H_{m-1}C][H^+]}{[H_mC]} \quad ...(109a)$$

$$H_{m-1}C \rightleftharpoons H_{m-2}C+H^+;\ K_{2C}^H=\frac{[H_{m-2}C][H^+]}{[H_{m-1}C]} \quad ...(109b)$$

$$HC \rightleftharpoons C+H^+;\ K_{mC}^H=\frac{[C][H^+]}{[HC]} \quad ...(109m)$$

$$M+C \rightleftharpoons MC;\ K_{1C}=\frac{[MC]}{[M][C]} \quad ...(110)$$

$$MC+C \rightleftharpoons MC_2;\ K_{2C}=\frac{[MC_2]}{[MC][C]} \quad ...(111)$$

$$MC_2+C \rightleftharpoons MC_3;\ K_{3C}=\frac{[MC_3]}{[MC_2][C]} \quad ...(112)$$

$$M+A+C \rightleftharpoons MAC;\ K_{1A1C}=\frac{[MAC]}{[M][A][C]} \quad ...(113)$$

$$M+B+C \rightleftharpoons MBC;\ K_{1B1C}=\frac{[MBC]}{[M][B][C]} \quad ...(114)$$

$$M+2B+A \rightleftharpoons MB_2A;\ K_{1A2B}=\frac{[MB_2A]}{[M][B]_2[A]} \quad ...(115)$$

$$M+2B+C \rightleftharpoons MB_2C;\ K_{2B1C}=\frac{[MB_2C]}{[M][B]^2[C]} \quad ...(116)$$

$$M+2A+C \rightleftharpoons MA_2C;\ K_{2A1C}=\frac{[MA_2C]}{[M][A]_2[C]} \quad ...(117)$$

$$M+2C+A \rightleftharpoons MC_2A;\ K_{1A2C}=\frac{[MC_2A]}{[M][C]^2[A]} \quad ...(118)$$

$$M+2C+B \rightleftharpoons MC_2B;\ K_{1B2C}=\frac{[MC_2B]}{[M][C]^2[B]} \quad ...(119)$$

$$M+A+B+C \rightleftharpoons MABC;\ K_{1A1B1C}=\frac{[MABC]}{[M][A][B][C]} \quad ...(120)$$

Therefore

$$C_M=[M]+[MA]+[MA_2]+[MA_3]+[MB]+[MB_2]+[MB_3]+[MC]+[MC_2]+[MC_3]+[MAB]+[MBC]+[MAC]+[MA_2B]+[MA_2C]+[MB_2C]+[MB_2A]+[MC_2A]+[MC_2B]+[MABC] \quad ...(121)$$

$$C_A=[H_nA]+[H_{n-1}A]+\cdots+[A]+[MA]+2[MA_2]+3[MA_3]+[MAB]+[MAC]+2[MA_2B]+2[MA_2C]+[MB_2A]+[MC_2A]+[MABC] \quad ...(122)$$

$$C_B=[H_lB]+[H_{l-1}B]+\cdots+[B]+[MB]+2[MB_2]+3[MB_3]+[MAB]+[MBC]+[MA_2B]+2[MB_2C]+2[MB_2A]+[MC_2B]+[MABC] \quad ...(123)$$

*In 1:1:1 mixture neither of the higher species, viz. 1:2:1 or 1:1:2 would be appreciable, and the formation constant for the equilibrium (71) can be evaluated for MAB.

$$C_C=[H_mC]+[H_{m-1}C]+\cdots+[C]+[MC]+2[MC_2]+3[MC_3]+[MBC]+[MAC]+[MA_2C]+[MB_2C]+2[MC_2A]+2[MC_2B]+[MABC] \quad ...(124)$$

$$aC_M=[H_{n-1}A]+2[H_{n-2}A]+\cdots+n[A]+n[MA]+2n[MA_2]+3n[MA_3]+[H_{l-1}B]+2[H_{l-2}B]+\cdots+l[B]+l[MB]+2l[MB_2]+3l[MB_3]+[H_{m-1}C]+2[H_{m-2}C]+\cdots+m[C]+m[MC]+2m[MC_2]+3m[MC_3]+(n+l)[MAB]+(l+m)[MBC]+(n+m)[MAC]+(2n+l)[MA_2B]+(2n+m)[MA_2C]+(2l+m)[MB_2C]+(2l+n)[MB_2A]+(2m+n)[MC_2A]+(2m+l)[MC_2B]+(n+l+m)[MABC] \quad ...(125)$$

Therefore

$$C_M(n+l+m-a)=a_1[A]+b_1[B]+c_1[C] \quad ...(126)$$

where

$$c_1=\frac{m[H^+]^m}{K^H_{1C}K^H_{2C}\cdots K^H_{mC}}+\frac{(m-1)[H^+]^{m-1}}{K^H_{2C}K^H_{3C}\cdots K^H_{mC}}+\cdots+\frac{[H^+]}{K^H_{mC}} \quad ...(127)$$

The equilibrium constants of the reactions (109)-(112) can be evaluated by the usual procedures as described earlier. In the reactions (113)-(119) the method of equilibrium (96) can be followed. Thus from equations (121)-(125) substituting the equilibrium constants:

$$[M]=a_2[A]/(1+K_{1B}[B]+K_{1B}K_{2B}[B]^2+K_{1B}K_{2B}K_{3B}[B]^3+K_{1C}[C]+K_{1C}K_{2C}[C]^2+K_{1C}K_{2C}K_{3C}[C]^3+K_{2B1C}[B]^2[C]+K_{2C1B}[C]^2[B]+K_{1B1C}[B][C]-K_{1A}K_{2A}[A]^2-2K_{1A}K_{2A}K_{3A}[A]^3-K_{2A1B}[A]^2[B]-K_{2A1C}[A]^2[C])$$

$$=b_2[B]/(1+K_{1A}[A]+K_{1A}K_{2A}[A]^2+K_{1A}K_{2A}K_{3A}[A]^3+K_{1C}[C]+K_{1C}K_{2C}[C]^2+K_{1C}K_{2C}K_{3C}[C]^3+K_{2A1C}[A]^2[C]+K_{2C1A}[C]^2[A]+K_{1A1C}[A][C]-K_{1B}K_{2B}[B]^2-2K_{1B}K_{2B}K_{3B}[B]^3-K_{2B1A}[B]^2[A]-K_{2B1C}[B]^2[C])$$

$$=c_2[C]/(1+K_{1B}[B]+K_{1B}K_{2B}[B]^2+K_{1B}K_{2B}K_{3B}[B]^3+K_{1A}[A]+K_{1A}K_{2A}[A]^2+K_{1A}K_{2A}K_{3A}[A]^3+K_{2A1B}[A]^2[B]+K_{2B1A}[B]^2[A]+K_{1A1B}[A][B]-K_{1C}K_{2C}[C]^2-2K_{1C}K_{2C}K_{3C}[C]^3-K_{2C1A}[C]^2[A]-K_{2C1B}[C]^2[B]) \quad ...(128)$$

where

$$c_2=\frac{[H^+]^m}{K^H_{1C}K^H_{2C}\cdots K^H_{mC}}+\frac{[H^+]^{m-1}}{K^H_{2C}K^H_{3C}\cdots K^H_{mC}}+\cdots+\frac{[H^+]}{K^H_{mC}}+1 \quad ...(129)$$

Further Eqs. (126) and (128) give Eq. (130)

$$T'_1[A]^4+T'_2[A]^3+T'_3[A]^2+T'_4[A]-T_5=0 \quad ...(130)$$

involving various known values from which T'_1, $T'_2,\cdots,T_5$ can be calculated. Thus after the determination of [A], [B] and [C], [MABC] can be evaluated as usual.

(iv) *Chelates involving more than three ligands* — The above method can be employed for other mixed ligand chelate equilibria also where more than three ligand molecules are attached with the metal ions. Eq. (130) may be written in the generalized form:

$$\sum_{m=1}^{m=n+1} S_m[A]^m = S_{n+2} \quad ...(131)$$

(where n is the number of ligand molecules associated with the metal ion, and $S_1, S_2 \ldots S_{n+2}$ are the various constants which may be evaluated from the titration data). For a mixed chelate system involving the ligands A, B, C, . . . etc., the free ligand concentration of one of the ligands A can be evaluated from Eq. (131). [B], [C], [D], etc., can be similarly evaluated. These may then be used for the determination of other quantities for the evaluation of equilibrium constants.

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References

1. Beck, M. T., *Chemistry of complex equilibria* (Van Nostrand, London), 1970.
2. Calvin, M. & Wilson, K. W., *J. Am. chem. Soc.*, **67** (1945), 2003.
3. Bjerrum, J., *Metal ammine formation in aqueous solution* (P. Haase & Son, Copenhagen), 1941.
4. Irving, H. M. & Rossotti, H. S., *J. chem. Soc.*, (1954), 2904.
5. Chaberek, S. & Martell, A. E., *J. Am. chem. Soc.*, **74** (1952), 5052; **77** (1955), 1477.
6. Nayan, R. & Dey, A. K., *Proc. 11th rare earth res. conf., Traverse City, Michigan (USA)*, 1974; *Proc. 12th rare earth res conf., Vall, Colorado (USA)*, 1976.
7. Nayan, R. & Dey, A. K., *Transition metal Chem.*, **1** (1976), 61; *J. coord Chem.*, (in press).
8. Nayan, R. & Dey, A. K., *J. inorg. nucl. Chem.*, **36** (1974), 2545.
9. Schwarzenbach, G., Willi, A. & Bach, R. O., *Helv. chim. Acta*, **30** (1947), 1303.
10. Schwarzenbach, G. & Ackermann, A., *Helv. chim. Acta*, **31** (1948), 1029.
11. Schwarzenbach, G., *Helv. chim. Acta*, **33** (1950), 947.
12. Chaberek, S., Courtney, R. C. & Martell, A. E., *J. Am. chem. Soc.*, **75** (1956), 2185.
13. Beck, M. T. & Görög, S., *Acta chim. hung.*, **22** (1960), 159.
14. Beck, M. T. & Görög, S., *J. inorg. nucl. Chem.*, **12** (1960), 353.
15. Österberg, R., *Acta chem. scand.*, **14** (1960), 471; **19** (1965), 1445.
16. Österberg, R., *Ark. Kemi.*, **25** (1966), 177.
17. Carey, G. H. & Martell, A. E., *J. Am. chem. Soc.*, **89** (1967), 2859.
18. Degischer, G. & Nancollas, G. H., *Inorg. Chem.*, **9** (1970), 1259.
19. Chidambaram, M. V. & Bhattacharya, P. K., *J. inorg. nucl. Chem.*, **32** (1970), 3271.
20. Sillén, L. G., *Acta chem. scand.*, **16** (1962), 159; **18** (1964), 1085.
21. Ingri, N. & Sillén, L. G., *Acta chem. scand.*, **16** (1962), 173.
22. Ingri, N. & Sillén, L. G., *Ark. Kemi.*, **23** (1964), 97.
23. Leussing, D. L., *Talanta*, **11** (1964), 189.
24. Sayce, I. G., *Talanta*, **15** (1968), 1397.
25. T. P. I. & Nancollas, G. H., *Inorg. Chem.*, **11** (1972), 2414.
26. Perrin, D. D., Sayce, I. G. & Sharma, V. S., *J. chem. Soc.*, A (1967), 1755.
27. Perrin, D. D. & Sharma, V. S., *J. chem. Soc.*, A (1968), 446.
28. Näsänen, R., Merilainen, P. & Lukkari, S., *Acta chem. scand.*, **16** (1962), 2384.
29. Näsänen, R. & Koskinen, M., *Suomen kemistilehti*, **B40** (1967), 23.